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14. ABSTRACT Dissolved organic matter (DOM) exported from rivers and intertidal marshes to coastal oceans typically contains high concentrations of light-absorbing molecules that can interfere with remote sensing of ocean color. This project quantitatively assessed the ability of coastal ocean bacteria to degrade and produce CDOM and investigated the synergistic interactions between bacterial degradation and photochemical processes in transforming CDOM in seawater and altering its optical properties. Optical properties (absorption spectra, EEMs), photoreactivity and biological lability of CDOM formed during the bacterial degradation of selected vascular plants and algae was used to asses the relative importance of terrestrial and marine organic matter as sources of CDOM.

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FINAL REPORT

GRANT #: N00014-98-1-0530

PRINCIPAL INVESTIGATOR: Mary Ann Moran

GRANT TITLE: Effects of Biological and Photochemical Degradation on the Optical Properties of CDOM Exported to Coastal Marine Environments

AWARD PERIOD: 1 April, 1999 – 31 March 2003

OBJECTIVES: Dissolved organic matter (DOM) exported from rivers and intertidal marshes to coastal oceans typically contains high concentrations of light-absorbing molecules that can interfere with remote sensing of ocean color. The specific objectives of this project were to quantitatively assess the ability of coastal ocean bacteria to degrade and produce CDOM; to investigate the synergistic interactions between bacterial degradation and photochemical processes in transforming CDOM in seawater and altering its optical properties; to compare susceptibility of CDOM from different source materials to degradation processes; and to provide quantitative mass-balance comparisons of biological vs. photochemical processes in CDOM removal under realistic irradiation schemes

APPROACH: Changes in the optical properties of CDOM due to biological and photochemical degradation were studied in laboratory and field experiments. For the laboratory studies, we investigated natural estuarine CDOM and model CDOM derived from degrading vascular plants and coastal phytoplankton (representing terrestrial and marine CDOM endmembers). Molecular biology techniques were employed to track microbial community composition during formation of CDOM from model terrestrial and marine source materials. Changes in CDOM concentrations and optical properties were quantified when the CDOM was subjected to both dark microbial degradation and irradiations with simulated sunlight. We investigated the potential influence of photocatalysis by iron as well as the role of particulates (through sorption processes) in modulating estuarine CDOM loss via photodegradation. In field studies of southeastern U.S. coastal areas (surface waters off Georgia and Florida), simultaneous measures of bacterial degradation, photochemical degradation, and optical properties of CDOM were carried out.

ACCOMPLISHMENTS:
Work during the first 12 months focused on assessing the variation in terrestrial CDOM end members with regard to biological and/or photochemical lability and optical properties. Research on an ONR-sponsored cruise on the Mississippi River plume in the Gulf of Mexico during June 2000 indicated the presence of two classes of CDOM in the Gulf of Mexico that exhibit distinct biological/photochemical lability: CDOM in the surface plume is susceptible to bleaching of color and photodegradation to biologically-labile photoproducts, while CDOM associated with the bottom of the chlorophyll maximum (i.e., produced in situ) is comparatively unreactive. Experiments in collaboration with Dr. Juanita Urban-Rich during the April 2001 (spring flood stage) ONR cruise demonstrated that bacterial/zooplankton interactions were important in the formation of CDOM. The first measurements of spectral quantum yields for photochemically-stimulated biological degradation of CDOM was accomplished during Year 1 for coastal Georgia locations. The spectral dependence for the quantum yields for combined photo- and biodegradation decrease exponentially in a remarkably similar fashion, suggesting that that common intermediates may be involved in both processes. Quantum yield spectra coupled with diffuse attenuation coefficients for downwelling irradiance were measured along a southeastern coastal U.S. transect from highly-productive to less-productive waters, to model the depth dependence and degradation fluxes of CDOM and examine the global significance of coastal DOM photodegradation.

Work during the second 12 months focused on assessing the optical properties of single-source CDOM produced during the degradation of vascular plants and algae; determining the biological availability and production of biologically labile photoproducts from single-source CDOM; characterizing the bacterial communities associated with the formation and degradation of CDOM from vascular plant and algal sources; and analyzing extensive field data sets of temporal and spatial variability of fluorescent DOM along the southeastern U.S. coast, including an analysis of variability in fluorescence quantum yield. Spectral and photochemical properties were also determined for water samples obtained at a series of depths during a June, 2001 cruise in the Florida Keys. Studies were initiated on sources and sinks of CDOM on particles.

Work during the final 12 month period focused on molecular biology-based analyses of the bacterial communities responsible for formation and degradation of CDOM from vascular plant and algal sources; completing and submitting a manuscript describing an improved method for using excitation-emission matrices of fluorescence spectra (EEMs) to evaluate within-estuarine changes in CDOM optical properties; completing analysis of spectroscopic, biological and photochemical data obtained during an ONR-sponsored CDOM cruise and contributing to preparation of a joint manuscript; completing research on sources and sinks of CDOM on particles, including work on temperature and UV effects on CDOM released from degrading seagrass and mangrove detritus and the effects of sorption to suspended sediments on optical properties of riverine CDOM.

CONCLUSIONS:

We developed a new method for eliminating Rayleigh and Raman scatter peaks from CDOM fluorescence data that provides much improved results in the quantitative analysis of EEMs compared to the conventional blank subtraction procedure. Modeling results and observed EEM spectral changes indicate that photoreactions, interacting with microbial transformations, have an important effect on the FDOM optical properties in estuaries. EEM analysis with careful scatter correction can provide a powerful tool for evaluating pathways for carbon cycling in estuaries. Optical properties (absorption spectra, EEMs), photoreactivity and biological lability of CDOM formed during the bacterial degradation of selected vascular plants and algae can be used to asses the relative importance of terrestrial and marine organic matter as sources of CDOM. Woody vascular material (oak and pine) is more resistant to biological transformation into colored matter than are non-woody sources, although these form labile photoproducts upon irradiation. Molecular fingerprints of bacterial communities indicate that CDOM from various sources converges to a similar suite of organic compounds during bacterial decomposition. Iron catalysis and reactive oxygen species can also be causal mechanisms for photochemical CDOM loss in estuaries. Potent oxidants (OH radicals) are produced when CDOM from the Mississippi River plume and estuaries of the southeastern U.S. are irradiated by sunlight and monochromatic UV radiation, and these radicals contribute to the reactions that cause CDOM photobleaching. CDOM fluorescence in five Georgia estuaries show changes related to mixing of ocean water with riverine water; both a dilution effect as well as chemical reactions with the seawater salts that increased fluorescence quantum yields are involved. CDOM transformations can affect fluorophore concentrations and spectra within the estuaries, but the relative importance of such transformations depends on residence time in the estuary.

SIGNIFICANCE:

Robust algorithms are necessary for the retrieval of CDOM signals from satellite absorbance data. The information being obtained in this project will increase understanding of how rapidly terrestrially-derived CDOM is degraded in coastal seawater, which mechanisms are most important in bringing about its removal, how DCOM degradation rates vary over time and space scales, and whether the mechanisms by which CDOM is removed leaves a signature in its optical properties. This study will also provide information about the variability of CDOM originating from various terrestrial endmembers with regard to removal rates and changes in optical properties

AWARD INFORMATION:

M. A. Moran: Promoted to full professor; Recipient of the National Oceanographic Partnership Program Award for Excellence, 2001; Selected as plenary lecturer, American Society for Limnology and Oceanography Annual Meeting, 2002

PUBLICATIONS AND PUBLISHED ABSTRACTS:

1. Opsahl, S. and R. G. Zepp. 2001. Photochemically-induced alteration of stable carbon isotope ratios ($\delta^{13}C$) in terrigenous dissolved organic carbon. Geophys. Res. Lett. 28: 2417-2420.
2. Miller, W. L., M. A. Moran, W. M. Sheldon, R. G. Zepp, and S. Opsahl. 2002. Determination of apparent quantum yield spectra for the formation of biologically labile photoproducts. Limnology and Oceanography 47: 343-352.
3. Hu, C., F. E. Muller-Karger, and R. G. Zepp. 2002. Absorbance, absorption coefficient, and apparent quantum yield: A comment on common ambiguity in the use of these optical concepts. Limnol. Oceanog. 47(4): 1261-1267.
4. Zepp, R.G. 2002. Solar ultraviolet radiation and aquatic carbon, nitrogen, sulfur and metals cycling. In: UV effects in aquatic organisms and ecosystems (E. W. Helbling and H. Zagarese, Eds), Comprehensive Series in Photosciences (D-P. Häder, G. Jori, series eds.), Royal Society of Chemistry, London, UK.
5. Zepp, R.G., T.V. Callaghan, and D.J. Erickson, Interactive effects of ozone depletion and climate change on biogeochemical cycles. In: Environmental effects of ozone depletion and its interactions with climate change: 2002 assessment. United Nations Environment Programme (UNEP), Nairobi Kenya, November 2002.
6. Zepp, R. G., M.A. Moran, E. M. White, and E. Stabenau. 2002. Photochemical and biological degradation of CDOM in waters from selected coastal regions of the southeastern United States. Eos Trans. AGU 83(4), OS 278 (published abstract for Ocean Sciences 2002)
7. Moran, M. A. and J. S. Covert. 2003. Photochemically mediated linkages between DOM and bacterioplankton. In: Aquatic Ecosystems: Interactivity of dissolved organic matter. (S. Findlay and R. Sinsabaugh, eds.) Academic Press.
8. Zepp, R. G., T. V. Callaghan, and D. Erickson. 2003. Interactive effects of ozone depletion and climate change on biogeochemical cycles. Photochem. Photobiol. *Sci.* 2: 51-61.
9. Kowalczuk, P., W. J. Cooper, R. F. Whitehead, M. J. Durako, and W. Sheldon. 2003. Characterization of CDOM in an organic-rich river and surrounding coastal ocean in the South Atlantic Bight. Aquat. Sci. 65:384-401.
10. White, E., Vaughan, P., and Zepp, R. 2003. Role of the photo-Fenton reaction in the production of hydroxyl radicals and photobleaching of colored dissolved organic matter in a coastal river of the southeastern United States. Aquatic Sciences 65: 402-414.
11. Zepp R. G. , M. A. Moran, and D. Koopmans. 2003. Photoreactivity of chromophoric dissolved organic matter (CDOM) derived from decomposition of various vascular plant and algal sources. Preprint Extended Abstract, Environmental Chemistry Division, 225th American Chemical Society National Meeting, New Orleans.
12. Zepp, R.G., W. M. Sheldon, and M. A. Moran. 2004. Dissolved organic fluorophores in southeastern U.S. coastal waters: Correction method for eliminating Rayleigh and Raman scattering peaks in excitation-emission matrices. Marine Chemistry, in press.
13. Chen, R. F., P. Bissett, P. Coble, R. Conmy, G. B. Gardner, M. A. Moran, X. Wang, M. L. Wells, P. Whelan, and R. G. Zepp. 2004. Chromophoric dissolved organic matter (CDOM) source characterization in the Louisiana Bight. Marine Chemistry, in press.

PRESENTATIONS

1. Zepp, R. G., E. Davis, S. Anderson, D. Santavy , L. Hansen, and K. Patterson. 2000. Role of DOM photoreactions in controlling UV exposure of coral assemblages in the Florida Keys. Invited lecture at the International Chemical Congress of Pacific Basin Societies, Pacifichem 2000, Honolulu, HI, Dec. 2000

2. Zepp, R. G. 2000. Effects of ozone depletion on global biogeochemical cycles. Invited presentation at annual meeting of the UNEP panel on effects of ozone depletion on the environment. Abisko, Sweden, August 2000.
3. Zepp, R. G. 2001. Light and aquatic chemistry: Influence of changing solar UV radiation on organic photoreactions in the environment. Invited lecture at the University of North Carolina Wilmington, January 2001.
4. Opsahl, S. and R. G. Zepp. 2001. Photochemically-induced transformations of dissolved organic matter in riverine waters. Invited lecture at the Am. Soc.of Limnol. Oceanog. 2001 Aquatic Sciences meeting Albuquerque NM, Feb. 2001.
5. Zepp, R. G. 2001. Photoreactions in surface waters and their role in biogeochemical cycles. Invited lecture at the Am. Soc.of Limnol. Oceanog. 2001 Aquatic Sciences meeting Albuquerque NM, Feb. 2001.
6. Anderson, S., R. Zepp, J. Machula, L. Hansen, G. Cherr, and E. Mueller. 2001. Assessing UV irradiance in Carribean reef coral and DNA damage in their coral and zooxanthellae. Presented at the Am. Soc.of Limnol. Oceanog. 2001 Aquatic Sciences meeting Albuquerque NM, Feb. 2001.
7. Moran, M. A. and R. G. Zepp. 2001. Interaction of biological and photochemical processes in the degradation of CDOM in coastal marine environments. 2001 update. Presentation at the ONR PI Meeting. Albuquerque NM, Feb. 2001.
8. Moran, M. A. 2001. Interaction of biological and photochemical processes in the degradation of terrestrial DOM in the coastal zone. Bedford Institute of Oceanography, Halifax, NS. (Invited presentation).
9. Zepp, R. G. 2001. Interactions of solar ultraviolet radiation and dissolved organic matter in freshwater and marine environments. Invited lecture at Lehigh University, March, 2001.
10. Zepp, R. G., H. Xie, M.A. Moran, and O. C. Zafiriou. 2001. Biological significance of UV-induced photoreactions of organic matter in aquatic environments. Annual Meeting of the Society of Environ. Toxicol. Chem., Baltimore, Md., Nov. 2001. (Invited presentation).
11. Zepp, R. G., M.A. Moran, E. M. White, and E. Stabenau. 2002. Photochemical and biological degradation of CDOM in waters from selected coastal regions of the southeastern United States. Presentation at AGU/ASLO Ocean Sciences: 2002 Meeting, Honolulu, February 2002.
12. Zepp, R. G. 2002. Changing solar radiation and aquatic biogeochemistry. University of Otago, Dunedin, New Zealand, Feb. 2002. (Invited presentation).
13. Zepp, R. G. 2002. Effects of ozone depletion on global biogeochemical cycles. Annual meeting of the UNEP panel on effects of ozone depletion on the environment. Wellington, New Zealand, February 2002. (Invited presentation).
14. Zepp, R. G. 2002. UV-CDOM interactions in coastal waters of the southeastern United States. University of Miami, Miami FL, May 2002. (Invited presentation).
15. Moran, M. A. and R. G. Zepp. 2002. Effects of biological and photochemical degradation on the optical properties of CDOM exported to coastal system. ONR CDOM Workshop, Woods Hole, MA. July 2002.
16. Chen, R. F., G. B. Gardner, M. A. Moran, R. Zepp, M. L. Wells, P. Bissett, R. Conmy, et al. CDOM source characterization in the Louisiana Bight. ASLO Annual Meeting. February 2003.
17. Zepp, R. G., M. A. Moran, and D. Koopmans. Photoreactivity of chromophoric dissolved organic matter (CDOM) derived from decomposition of various vascular plant and algal sources. American Chemical Society Annual Meeting. New Orleans, LA. March 2003.
18. White, E. M. P.P. Vaughan, and R. G. Zepp. Photochemical production of hydroxyl radical in natural waters: The role of iron and dissolved organic matter. American Chemical Society Annual Meeting. New Orleans, LA. March 2003.
19. Xie, H., O. C. Zafiriou, W-J. Cai, R. G. Zepp, and Y. Wang. Effects of sunlight on carboxyl content of dissolved organic matter in the Satilla River of Georgia, United States. American Chemical Society Annual Meeting. New Orleans, LA. March 2003.